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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition giving a cured product which ensures practical curability and recovery properties and exhibits mechanical properties of high strength and high elongation.

SOLUTION: The curable composition is characterized by comprising (A) an organic polymer having at least one silicon-containing group which has a hydroxy or hydrolyzable group bonded to the silicon atom and is crosslinkable by forming a siloxane bond, and (B) one or more metal salts of a carboxylic acid selected from calcium carboxylate, vanadium carboxylate, iron carboxylate, titanium carboxylate, potassium carboxylate, barium carboxylate, manganese carboxylate, nickel carboxylate, cobalt carboxylate, and zirconium carboxylate.

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CLAIMS

[Claim(s)]

[Claim 1] (B) A hardenability constituent given in any 1 paragraph of Claims 1-6 to which carboxylic acid iron of an ingredient uses as the main ingredients carboxylic acid metal salt expressed with the general formula (4) or (5), and carboxylic acid cobalt of the (B) ingredient uses as the main ingredients carboxylic acid metal salt expressed with a general formula (11).

Fe(OGOR)₂ (4)
Fe(OCOR)₃ (5)
Co(OCOR)₂ (11)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group which has the third class carbon or quaternary carbon which adjoins a carbonyl group, and include a carbon carbon double bond.)

It may be.

[Claim 8] (B) The hardenability constituent according to any one of claims 1 to 7 whose carboxylic acid metal salt of an ingredient is the carboxylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 °C or less.

[Claim 9] (B) The hardenability constituent according to any one of claims 1 to 7 which is the carboxylic acid metal salt which has an acid radical of carboxylic acid whose carbon numbers in which carboxylic acid metal salt of an ingredient contains carbon of a carbonyl group are 2-17.

[Claim 10] (B) A hardenability constituent given in any 1 paragraph of Claims 1-8 which are metal salt of a carboxylic acid group content compound in which carboxylic acid metal salt of an ingredient is chosen from 2-ethylhexanoic acid, neo decanoic acid, or naphthenic acid.

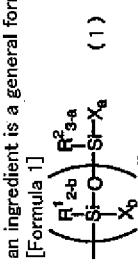
[Claim 11] (A) A hardenability constituent given in any 1 paragraph of Claims 2-10 containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 - 20 weight sections to ingredient 100 weight section.

[Claim 12] (A) A hardenability constituent containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient to ingredient 100 weight section.

[Claim 13] (C) The hardenability constituent according to claim 1 which becomes considering an amine compound as an essential ingredient as an ingredient.

[Claim 14] (A) A number average molecular weight is within the limits of 500-50,000, and an organic polymer of an ingredient is a general formula to an end and/or a side chain of a main chain (1). :

[Formula 1]



(R¹ and R² among a formula) They are an alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R²)₃SiO independently, respectively. — (R¹) respectively — independent — the substitution of the carbon numbers 1-20, or an unsubstituted hydrocarbon group — it is — it is the Tori ORGANOCO siloxy group shown. X is a hydroxyl group or a hydrolytic basis independently, respectively, a is 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0. m — the integer of 0, or 1-19 — it is — the hardenability expressed.

[Claim 4] The hardenability constituent according to claim 3, wherein X is an alkoxy group.

[Claim 5] (A) A hardenability constituent given in any 1 paragraph of Claims 1-4 whose organic polymers of an ingredient are a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[Claim 6]

The hardenability constituent according to claim 5 which is a polymer, wherein said saturated hydrocarbon system polymer has a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

[Claim 7]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001] In this invention, it has the hydroxyl group or hydrolytic basis combined with the silicon atom, and a siloxane bond is formed. Therefore, it is related with the hardenability constituent containing the organic polymer which has a silicon content group (henceforth a "reactive silicon group") which can construct a bridge.

[Background of the Invention]

[0002] It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the interesting character in which construct a bridge by formation of the siloxane bond accompanied by the hydrolysis reaction of a reactive silicon group, etc., and a rubber-like hardened material is obtained with hygroscopic surface moisture etc. also in a room temperature.

[0003]

In the polymer which it has, these reactive silicon groups a polyoxyalkylene series polymer and a polyisobutylene system polymer, It is indicated by JP,S52-73998,A, JP,H5-125272,A, JP,S63-6003,A, JP,S63-6041,A, JP,H1-38407,A, JP,H8-231758,A, etc. Especially a polyoxyalkylene series polymer and a polyisobutylene system polymer are already produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.

[0004]

When an organic polymer is a saturated hydrocarbon system polymer especially, since it excels in heat resistance, a water resisting property, weatherability, etc., if the hardened material obtained is used for a structural sealing material, the sealing material for multiple glass, etc., is effective. The isobutylene system polymer which has a repeating unit which furthermore originates in isobutylene 50% of the weight or more in a total amount is preferred as a sealant aiming at moisture proof from especially the thing to excel in low moisture permeability and low gas permeability.

[0005] Such a sealing material generally fills up the joined part and crevice between various members, the flatter nature to the use part ranging from being used to a long period of time in order to give watertight and airtightness becomes very important, and revealing sufficient elongation and intensity is called for.

[0006]

Amine compounds, such as lauryl amine, are used together as a co-catalyst in many cases for the purpose of a silanol condensation catalyst being used for bridge construction hardening of an organic polymer which, on the other hand, has such a reactive silicon group, and also accelerating a condensation reaction. As such a silanol condensation catalyst, divalent tin, such as octyltin ethylhexanoic acid) tin, The tin series catalyst represented by tetravalent tin, such as dibutyltin bisacetone, is used widely, and when the movement of the part which places especially a sealing material is large, since the hardened material which has stability is obtained, many divalent tin is used.

[0007]

However, when octyl acid tin which is divalent tin, for example is used together with the amine compound of a co-catalyst and is used as a curing catalyst of the (A) ingredient, the intensity and elongation of a hardened material which are acquired may be insufficient, and an improvement of the further physical properties is desired.

[0008] Although most is a dibutyltin type, the latter tetravalent tin series catalyst being used now, While the hardened material obtained has emollience, i.e., having the character to follow to the long-term stress change from the outside and fast curability, it is broadly used from the ability to apply as a curing catalyst of 1 liquid mold-curing nature constituent. However, since toxicity in case a small amount of tributyltin contains in this is regarded as questionable, development of the silanol condensation catalyst of a non-tin series is desired.

[0009] In JP,S35-2795,B, JP,S32-3742,B, JP,S35-9639,B, JP,S37-3271,B, etc. As a curing catalyst of an organopoly(alkylene constituent), the carboxylic acid metal salt of various kinds of non-tin is indicated with carboxylic acid of tin. As an example in which the carboxylic acid metal salt of non-tin was used for the curing catalyst of the constituent which, on the other hand, contains the organic polymer which has a reactive silicon group. Although there were carboxylic acid bismuth (JP,H5-39428,A, JP,H5-12860,A) and carboxylic acid cerium (JP,2000-313814,A), there was no example broadly examined in various carboxylic acid metal salt until now.

[Patent documents 1] JP,S52-73998,A
 [Patent documents 2] JP,H5-125272,A
 [Patent documents 3] JP,H3-72527,A
 [Patent documents 4] JP,S63-6003,A
 [Patent documents 5] JP,S63-6041,A
 [Patent documents 6] JP,H1-38407,A
 [Patent documents 7] JP,H8-231758,A
 [Patent documents 8] JP,S35-2795,B
 [Patent documents 9] JP,S32-3742,B
 [Patent documents 10] JP,S35-9639,B
 [Patent documents 11] JP,S37-3271,B, etc.
 [Patent documents 12] JP,H5-39428,A
 [Patent documents 13] JP,H9-12860,A
 [Patent documents 14] JP,2000-313814,A
 [Description of the Invention]
 [Problem(s) to be Solved by the Invention]

[0010] The purpose of this invention is as follows. Have practical hardenability and stability with a good hardened material obtained. Provide a hardenability constituent useful as the structural sealing material asked especially for high durability, the sealing material for multiple glass, the moisture seal material used for an electric electronic component, adhesives, etc. from revealing the outstanding intensity and elongation.

[Means for Solving the Problem]

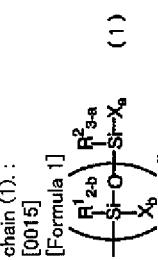
[0011] In order that this invention persons may solve such a problem, as a result of inquiring, as a curing catalyst of the (A) ingredient Carboxylic acid calcium, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, By using one or more sorts of carboxylic acid carboxylic acid cobalt, and a carboxylic acid zirconium, Securing moderate hardenability and stability, it finds out revealing high intensity and the physical properties of high elongation compared with a case where octyl acid tin is used as a curing catalyst, and came to complete this invention.

[0012] Namely, this invention has a hydroxyl group or a hydrolytic basis combined with the (A) silicon atom, It is related with a hardenability constituent containing one or more sorts of carboxylic acid metal salt chosen from an organic polymer, (B) carboxylic acid iron, and carboxylic acid cobalt which have at

least one silicon content group which can construct a bridge by forming a siloxane bond. [0013] An amine compound is related with the aforementioned hardenability constituent which becomes as an essential ingredient as a (C) ingredient.

[0014]

As a desirable embodiment, a number average molecular weight is within the limits of 500–50,000, and an organic polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main chain (1):



As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is metal salt of a carboxylic acid group content compound chosen from 2-ethylhexanoic acid, neo decanoic acid, or naphthenic acid. [0023]

It is related with a hardenability constituent given in said either containing the (B) ingredient of quantity which serves as 0.005–5 weight section by metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as a desirable embodiment. [0024]

It is related with a hardenability constituent given in said either containing the (B) ingredient of quantity which serves as 0.005–5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01–20 weight sections to (A) ingredient 100 weight section as a desirable embodiment. [0025]

[Best Mode of Carrying Out the Invention]

Hereafter, this invention is explained in detail.

[0026]

Restriction in particular does not have a principal chain skeleton of an organic polymer which has a reactive silicon group used for this invention, and it can use a thing with various kinds of principal chain skeletons.

[0027]

Specifically A polyoxyethylene, polyoxypropylene, polyoxy butylene, Polyoxy tetramethyl, a polyoxyethylene polyoxypropylene copolymer, Or polyoxyethylene series polymers, such as a polyoxypropylene polyoxy butylene copolymer; An ethylene-propylene system copolymer, The copolymer of polyisobutylene, isobutylene, isoprene, etc., polyisobutylene, A copolymer with polyisoprene, isoprene or butadiene, acrylonitrile, styrene, etc., Hydrocarbon system polymers, such as a hydrogenation polybutadiene or these polyolefine system polymers; Condensation with dibasic acid, such as adipic acid, and glycol. Or the polyester system polymers; Condensation with the ring opening polymerization of lactone; The polyacrylate ester produced by carrying out the radical polymerization of the monomers, such as ethyl acrylate and butyl acrylate, Vinyl-base polymers, such as an acrylic ester system copolymer with acrylic ester, such as ethyl acrylate and butyl acrylate, vinyl acetate, acrylonitrile, methyl methacrylate, styrene, etc.; A vinyl monomer is polymerized to said organic polymer. Graft polymer; obtained.

Polysulfide system polymers; Nylon 610 by the condensation polymerization of the nylon 6 by the ring opening polymerization of epsilon caprolactam, hexamethylenediamine, Nylon 66 by the condensation polymerization of adipic acid and hexamethylene diamine, and sebacic acid, Nylon 11 by the condensation polymerization of epsilon-aminoundecanoic acid, Condensation polymerization is carried out from polyamide system polymer, for example, bisphenol A, and the carbonyl chlorides which have a two or more-ingredient ingredient among Nylon 12 by the ring opening polymerization of epsilon-amino RAURO lactam, and the above-mentioned nylon, such as copolyamide. The polycarbonate system polymer manufactured; a diallyl phthalate system polymer etc. are illustrated. [0028]

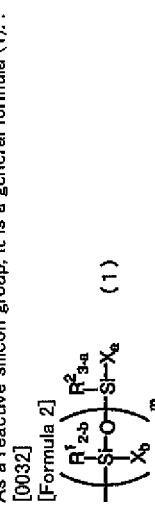
Since acquisition and manufacture are easy among polymers with the above-mentioned principal chain skeleton, a polyoxyethylene series polymer, a hydrocarbon system polymer, a polyester system polymer, a vinyl system copolymer, a polycarbonate system polymer, etc., are preferred. A saturated hydrocarbon system polymer, and a polyoxyethylene series polymer and a vinyl system copolymer have a comparatively low glass transition temperature, and their hardened material obtained is especially preferred from excelling in cold resistance. [0029]

As a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention, the reactive silicon group content saturated hydrocarbon system polymer derived from saturated hydrocarbon system polymers, such as polyisobutylene, hydrogenation polybutadiene, and hydrogenation polyisoprene, is raised. [0030]

The reactive silicon group contained in the organic polymer which has a reactive silicon group is a basis which can construct a bridge by formation of the siloxane bond which is a reaction which has

the hydroxyl group or hydrolytic basis combined with the silicon atom, and is accelerated with the carboxylic acid metal salt which is the (B) ingredient.

[0031] As a reactive silicon group, it is a general formula (1):



[0032]

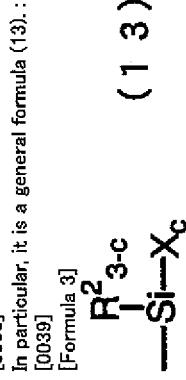
(R¹ and R² among a formula) They are an alkyl group of the carbon numbers 1~20, an aryl group of the carbon numbers 6~20, an aralkyl group of the carbon numbers 7~20, or (R')³SiO independently, respectively. — (R') respectively — independent — substitution of the carbon numbers 1~20, or an unsubstituted hydrocarbon group — it is — it is the Tori ORGANO siloxy group shown. X is a hydroxyl group or a hydrolytic basis independently, respectively. a is 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0. m — an integer of 0, or 1~19 — it is — a basis expressed is raised.

[0033] Among these, although an alkoxy group, an amido group, and an aminoxy group are preferred, a point of hydrolytic nature being quiet and being easy to deal with it to especially an alkoxy group is preferred.

[0034] A hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1~3 ranges, and (a+sigmab) has 1~5 preferred ranges. When a hydrolytic basis and a hydroxyl group join together in [two or more] a reactive silicon group, they may be the same and may differ.

[0035] Although a silicon atom which forms a reactive silicon group is one or more pieces, in the case of a silicon atom connected by siloxane bond etc., it is preferred that they are 20 or less pieces.

[0036]



[0037]

(R² and X are the same as the above among a formula.) c is an integer of 1~3. Since the reactive silicon group expressed is easy to receive, it is preferred.

[0038]

In the above-mentioned general formula (13), Tori alkoxy silyl groups, such as a methoxy group, an ethoxy basis, a propoxy group, and an isopropoxy group, is mentioned for X as an example in case c is 3. In the above-mentioned general formula (13), as an example of R² in case c is not 3. For example,

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cycloalkyl groups, such as alkyl groups, such as a methyl group and an ethyl group, and a cyclohexyl group, Aralkyl groups, such as aryl groups, such as a phenyl group, and benzyl, the Tori ORGANO siloxy group R' is indicated to be by SiO which is a methyl group, a phenyl group, etc. (R'), etc. are mentioned. In these, the point that the activity of a hydrolysis reaction is high to especially a methyl group is preferred.

[0042]

As more concrete illustration of a reactive silicon group, a trimethoxysilyl group, a triethoxysilyl group, a triisopropoxy silyl group, a dimethoxymethylsilyl group, and a diisopropoxymethylsilyl group are mentioned. Its activity is high, and since especially the trimethoxysilyl group can reduce quantity of carboxylic acid metal salt which is the (B) ingredient, it is preferred.

[0043]

What is necessary is just to perform introduction of a reactive silicon group by a publicly known method. That is, the following methods are mentioned, for example.

[0044]

(b) Make an organic compound which has an active group and an unsaturation group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, in a molecule to this functional group react, and obtain an organic polymer containing an unsaturation group. Or an unsaturation group content organicity polymers is obtained by copolymerization with an unsaturation group content epoxy compound. Subsequently, hydrosilane which has a reactive silicon group is made to act on an acquired resultant, and it hydrosilylates.

[0045]

(**) Make a compound which has a sulphydryl group and a reactive silicon group react to an organic polymer containing an unsaturation group produced by making it be the same as that of the (b) method.

[0046]

(**) Make a compound which has a functional group which has functional groups, such as a hydroxyl group, an epoxy group, and an isocyanate group, in a molecule to this functional group react.

[0047]

A method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group react to an end a method of (b) or among (**) is from points, like a manufacturing cost becomes low in the above method is preferred.

[0048]

(b) As an example of hydrosilane compound used in a method. For example, trichlorosilane, trimethoxysilane, chlorosilane, dimethylchlorosilane, Halogenation Silang like phenyl dichlorosilane, methyl dimethoxysilane, methyl acetoxysilane, The alkoxysilane like phenyl Triethoxysilane, methyl diethoxysilane, The acyloxy silanes like a phenylacetoxysilane; although the KETOKISHI mate silanes like bis(dimethyl KETOKISHI mate)methylsilane and bis(cyclohexyl KETOKISHI mate)methylsilane are raised, it is not limited to these. Among these, Halogenation Silang and alkoxysilane are especially preferred from points, like availability and hydrolysis reaction nature are high.

[0049]

(**) Although a method of introducing into an unsaturation binding site of an organic polymer a compound which has a sulphydryl group and a reactive silicon group as a synthetic method by a radical addition reaction under a radical initiator and/or radical source-of-release existence for example, etc. are mentioned, it is not limited in particular. As an example of a compound of having said sulphydryl group and a reactive silicon group. For example, although gamma-mercaptopropyl propyltrimethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercaptopropylmethyl diethoxysilane, etc. are raised, it is not limited to these.

[0050]

(**) Although a method etc. which are shown in JP,H3-47825,A are mentioned, for example as a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group reacting to an end among synthetic methods, it is not limited in

3. In the above-mentioned general formula (13), as an example of R² in case c is not 3. For example,

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particular. As an example of a compound of having said isocyanate group and a reactive silicon group. For example, although gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, gamma-isocyanate propyl triethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, etc. are raised, It is not limited to these.

[0051]

As for a silane compound which three hydrolytic bases have combined with one silicon atoms, such as trimethoxysilane, disproportionation may advance. If disproportionation progresses, a remarkable dangerous compound [like] which is dimethoxysilane will arise. However, such disproportionation advances in neither gamma-mercaptopropyltrimethoxysilane nor gamma-isocyanate propyltrimethoxysilane. For this reason, when three hydrolytic bases, such as a trimethoxysil group, use a basis combined with one silicon atom as a silicon content group, it is preferred to use a synthetic method of (***) or (****).

[0059] *** is mentioned. The principal chain skeleton of a polyoxalkylene series polymer may consist of one kind of repeating unit, and may consist of two or more kinds of repeating units. When used especially for sealant etc., it is desirable from that what comprises the polymer which uses a polyoxalkylene system polymer as the main ingredients is amorphous, or the point which is hypoviscosity comparatively.

as trimethoxysilane, disproportionation may advance. If disproportionation progresses, a remarkable dangerous compound [like] which is dimethoxysilane will arise. However, such disproportionation advances in neither gamma-mercaptop trimethoxysilane nor gamma-isocyanate propyltrimethoxysilane. For this reason, when three hydrolytic bases, such as a trimethoxysilyl group, use a basis combined with one silicon atom as a silicon content group, it is preferred to use a synthetic method of (**) or (**).

Pat. No. 3427334 item, The polymerizing method by a composite metal cyanide complex catalyst

(A) A number average molecular weight of an organic polymer which is an ingredient, In polystyrene conversion in GPC (gel permeation chromatography), it is preferred that it is 500 to about 50,000, and about 1,000 to 30,000 liquefied thing which is, carries out and has mobility is especially preferred from points, such as the number of dealing with it. If sufficient rubber elasticity is not obtained and 50,000 is exceeded, such as a number average molecular weight, is less than 500, since it is lacking in mobility and handling is difficult for it, at ordinary temperature, it is not desirable.

ingredients, such as a urethane bond ingredient, may be included in the range which does not spoil an effect of this invention greatly.

more pieces, and it is preferred that there are 1.5 pieces. Since it will become weak firmly and will become scarce at rubber elasticity if hardenability becomes insufficient, good rubber elasticity may not no longer be obtained, if the number of reactive silicon groups contained in a molecule will be less than one pieces, and five pieces are exceeded, it is not desirable.

[0055] Said polyoxvalylenes series polymer is a general formula intrinsically (14):

14 (1) $\text{P}^3-\text{O}-$

[0057] (among a formula, R^3 is a divalent organic group and is the straight chain shape or the branching alkylene group of the carbon numbers 1-14) — it being a polymer which has a repeating unit shown and, R_3 in a general formula (14) has the carbon numbers 1-14, and also preferred straight chain shape or branched state alkylene group of 2-4. As the example of the repeating unit shown by a

silicon group used in this invention, (V), wherein an organic compound of the carbon number 3 to 10 is attached to the silicon atom.

(2) After making olefin series, such as butadiene and isoprene, nonopolymerize or catalyze out copolymerization to the above-mentioned olefinic compound, can obtain by a method of hydrogenating, but. Since an isobutylene system polymer and a hydrogenation polybutadiene system polymer tend to introduce a functional group into an end, and tend to control a molecular weight and can increase the number of end functional groups, they are preferred.

[0066] All the monomeric units may be formed from an isobutylene unit, and an isobutylene system polymer is [in an isobutylene system polymer] desirable, and a monomeric unit which has isobutylene and copolymeric may be especially contained in 10 or less % of the weight of the range preferably 30 or 100 in case the number of the monomeric group, and are preferable.

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less % of the weight still more preferably 50 or less % of the weight. In an isobutylene system polymer, when content of a monomeric unit which has isobutylene and copolymeric exceeds 50 % of the weight, since characteristic physical properties, such as high weatherability, high heat resistance, low moisture permeability, etc. resulting from an isobutylene skeleton, are not fully revealed, it is not

[0067] As such a monomer component, an olefin of the carbon numbers 4-12, vinyl ether, an aromatic vinyl compound, vinylsilane, and arylsilane are raised, for example. As such a copolymer component, for example 1-butene, 2-butene, A 2-methyl-1-butene, a 3-methyl-1-butene, a pentene, 4-methyl-1-pentene, A hexene, a vinylcyclohexene, the methyl vinyl ether, ethyl vinyl ether, isobutylvinyl ether, styrene, alpha-methylstyrene, dimethylstyrene, Monochlorostyrene, dichlorostyrene, beta-pinene, indene, vinyl trichlorosilane, Vinyl methylid chlorosilane, vinylidenechlorosilane, vinyl dimethoxysilane, divinyl dichlorosilane, divinyl dimethoxysilane, Divinyl dimethylsilane, the 1,3-diviny-1,1, and 3,3-tetramethyl disiloxane, TORIBI nitr methylsilane, a tetravinyl silane, allyltrichlorosilane, Allyl methylid chlorosilane, allyldimethylchlorosilane, allyldimethyl methoxysilane, allyl trimethylsilane, diaryl dichlorosilane, diaryl dimethoxysilane, diaryl dimethylsilane, gamma-methacryloyl oxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane etc. are raised.

[0068] As a monomeric unit which has isobutylene and copolymeric among the above, if vinylsilane and arylsilane are used, a basis which silicon content increases and can act as a silane coupling agent will increase, and the adhesive property of a constituent obtained will improve.

[0069] Other monomeric units may be made to contain besides a monomeric unit used as the main ingredients like a case of the above-mentioned isobutylene system polymer in a hydrogenation polybutadiene system polymer or other saturated hydrocarbon system polymers.

To a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention. A little monomeric units in which an after-polymerization double bond like polyene compounds, such as butadiene and isoprene, remains in the range in which the purpose of this invention is attained may be made to contain in 1 or less % of the weight of the range preferably especially 5 or less % of the weight still more preferably 10 or less % of the weight.

[0071] A saturated hydrocarbon system polymer which has these reactive silicon groups can be independent or can be used together two or more sorts.

A process of a saturated hydrocarbon system polymer which has a reactive silicon group next is explained.

[0073]

An isobutylene system polymer which has a reactive silicon group in molecular chain terminals among isobutylene system polymers which have a reactive silicon group, an end organic-functions type obtained by the polymerizing method (cationic polymerization method using a specific compound combining and [which is called iniphor] and a chain transfer agent) called iniphor method -- it can manufacture preferably using a whole end organic-functions type isobutylene system polymer. As a process of a saturated hydrocarbon system polymer which has a reactive silicon group, For example, general formula (15) after obtaining polyisobutylene which has an unsaturation group at the end by dehydrohalogenation reaction of an end of a polymer which has third class carbon-chlorine combination obtained by a polymerization reaction, the reaction of an end of a polymer and allyl

trimethylsilane which have third class carbon-chlorine combination, etc.:

(15)

[0074] [Formula 6]

$$\begin{array}{c}
 R_{3,4}^2 \\
 | \\
 \left(\begin{array}{c} R^1_{2,6} \\ | \\ \text{Si} \end{array} \right) - \text{O} - \text{Si} - \text{X}_8 \\
 | \\
 \text{H} \quad \left(\begin{array}{c} X_6 \\ | \\ \text{Si} \end{array} \right) \\
 \end{array}$$

[0075] $(R^1, R^2, X, m, a, b$ are the same as the above among a formula.) — the hydrosilane compound (this compound is a compound which the hydrogen atom combined with the basis expressed with a general formula (1)) expressed — desirable — general formula (16):

$$\text{H}-\overset{\overset{\text{R}^2}{\text{Si}}}{\underset{\text{3-c}}{\text{---}}}-\text{X}_c \quad (16)$$

[0077] (R², X, and c are the same as the above among a formula.) — it can obtain by the reaction (hydrosilylation reaction) to which the hydrosilane compound expressed is made to add using a platinum catalyst

[0078] As a hydrosilane compound, for example Trichlorosilane, methylid chlorosilane, Halogenation Silane like dimethylchlorosilane and phenyl dichlorosilane; Trimethoxysilane, Triethoxysilane, Methyl diethoxysilane, methyl dimethoxysilane, The alkoxy silane like phenyl dimethoxysilane; Methyl acetoxysilane, The acyloxy silanes like a phenyldiacetoxysilane, although the KETOKISHI mate silane like bis(dimethyl KETOKISHI mate)methylsilane and bis(cyclohexyl KETOKISHI mate)methylsilane are raised, it is not limited to these. Among these, halogenation Silan and alkoxy silane are preferred especially in respect of the ease of acquisition, etc.

[0078] Such a manufacturing method is indicated in each gazette of JP,4-69659,B, JP,7-108928,B, JP,63-254149,A, JP,64-22904,A, and the patent No. 2539445, for example.

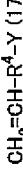
[0080] An isobutylene system polymer which has a reactive silicon group in a chain side chain is manufactured by adding and carrying out copolymerization of the vinylsilane and arylsilane which has a reactive silicon group into a monomer containing isobutylene.

In the case of a polymerization reaction which manufactures an isobutylene system polymer which has a reactive silicon group in molecular chain terminals. After carrying out copolymerization of the vinylsilane and arylsilane etc. which have a reactive silicon group in addition to an isobutylene monomer which is the main ingredients, an isobutylene system polymer which has a reactive silicon group in an end and a chain side chain is manufactured by introducing a reactive silicon group into a reactive silicon group into a monomer containing isobutylene.

[0082] As the vinylsilane which has a reactive silicon group, and arylsilane, For example, vinyl trichlorosilane, vinyl methyl chlorosilane, vinyl dimethylchlorosilane, Vinyl dimethylmethoxysilane, divinyl dichlorosilane, divinyl dimethoxysilane, Allyl trichlorosilane, Allyl methyl chlorosilane, allyl dimethylchlorosilane, Allyl dimethylmethoxysilane, Allyl dimethyl methoxysilane, diaryl dichlorosilane, diaryl dimethoxysilane, gamma-methacryloyl trimethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl methyl trimethoxysilane.

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polymer as oxy metal groups, such as $-\text{ONa}$ and $-\text{OK}$, first, for example :



Halogen atoms, such as a chlorine atom, a bromine atom, and iodine atoms, and R^4 are among [type, and Y is $-\text{R}^5$, $-\text{R}^5-\text{OCO}-$, or $-\text{R}^5-\text{OCO}-\text{CO}$. (R^5 is a divalent hydrocarbon group of the carbon numbers 1-20, and) an alkylene group, a cyclo alkylene group, an allylene group, and an aralkylene group — it is desirable — by a divalent organic group shown. — It can obtain by making an organic halogenated compound shown by especially a divalent basis chosen from CH_2^2 and $-\text{R}''-\text{C}_6\text{H}_4-\text{CH}_2$ (R'' is a hydrocarbon group of the carbon numbers 1-10) being preferred] react.

[0084] As a method of using terminal hydroxyl groups of an end hydroxy hydrogenation polybutadiene system polymer as a oxy metal group, A method of making it react to alkaline-water oxides, such as Na , metal alkoxide NaOH like metal hydride NaOCH_3 like alkali metal K , and KOH , etc. is raised.

[0085] Although an end olefin hydrogenation polybutadiene system polymer with the almost same molecular weight as an end hydroxy hydrogenation polybutadiene system polymer used as a starting material is obtained in said method. Before making an organic halogenated compound of a general formula (17) react to obtain a polymer of the amount of Polymer Division more, at the time, such as a methylene chloride, bis(chloromethyl)benzene, and bis(chloromethyl)ether. If it is made to react to an organic halogenated compound which can increase a molecular weight, if it is made to react to a multivalent organic halogenated compound which contains two or more halogen in one molecule, and is shown by a general formula (17) after that, A hydrogenation polybutadiene system polymer which is the amount of Polymer Division more, and has an olefin group at the end can be obtained.

[0086] As an example of an organic halogenated compound shown by said general formula (17), For example, an allyl chloride, an allyl star's picture, vinyl(chloromethyl) benzene, Allyl(chloromethoxy) benzene, allyl (bromomethyl) benzene, Although allyl (chloromethyl) ether, allyl(chloromethoxy) benzene, 1-buteneyl (chloromethyl) ether, 1-hexeneyl(chloromethoxy) benzene, allyloxy (chloromethyl) benzene, etc. are raised, it is not limited to them. Among these, an allyl chloride is cheap, and since it moreover reacts easily, it is desirable.

[0087] Introduction of a reactive silicon group to said end olefin hydrogenation polybutadiene system polymer may be manufactured by carrying out an addition reaction using a platinum system catalyst in a hydrosilane compound like a case of an isobutylene system polymer which has a reactive silicon group in molecular chain terminals.

[0088] When a saturated hydrocarbon system polymer which has a reactive silicon group as mentioned above does not contain substantially an unsaturated bond which is not an aromatic ring in a molecule, Compared with a sealing agent etc. which consist of a conventional rubber system polymer like an organic system polymer or an oxalkylene system polymer which has an unsaturated bond, a weatherability becomes good remarkably. Since this polymer is a hydrocarbon system polymer, its water resisting property is good, and a low hardened material of humidity permeability is obtained.

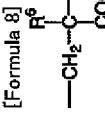
[0089] An organic polymer which has these reactive silicon groups may be used alone, and may be used together two or more sorts. Specifically, a polyoxalkylene series polymer which has a reactive silicon group, a saturated hydrocarbon system polymer which has a reactive silicon group, a vinyl-base polymer which has a reactive silicon group, and an organic polymer which blends two or more sorts chosen from a group, ** and others, can also be used.

[0090] A manufacturing method of an organic polymer which blends a polyoxalkylene series polymer which has a reactive silicon group, and a vinyl-base polymer which has a reactive silicon group, Although indicated by JP.59-122541,A, JP.63-112642,A, JP.H6-172631,A, JP.H11-116763,A, etc., it is not limited to in particular these.

[0091]

A desirable example has a reactive silicon group and a chain is a following general formula substantially (18). :

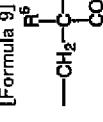
[0092]



[0093]

the acrylic ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with a hydrogen atom or a methyl group, and R^7 show the alkyl group of the carbon numbers 1-8 among a formula, as for R^6 (meta-), and following general formula (9).

[0094]



[0095]

(— the inside of a formula, and R^8 — the same — R^8 shows a with a carbon numbers of ten or more alkyl group —) to the copolymer which consists of an acrylic ester monomer unit which has a with a carbon numbers of ten or more expressed alkyl group (meta-). It is the method of blending and manufacturing the polyoxalkylene series polymer which has a reactive silicon group. Acrylic acid (meta) expresses acrylic acid and/or methacrylic acid with the above-mentioned expressive form.

[0096]

as R^7 of said general formula (18) — the carbon numbers 1-8 of a methyl group, an ethyl group, a propyl group, n-butyl group, t-butyl group, a 2-ethylhexyl group, etc. — desirable — 1-4 — an alkyl group of 1-2 is raised still more preferably. An alkyl group of R^7 may be independent and may be mixed two or more sorts.

[0097]

as R^8 of said general formula (19) — ten or more carbon numbers of a lauryl group, a tridecyl group, a octyl group, a stearyl group, a behenyl group, etc. — usually — 10-30 — a long-chain alkyl group of 10-20 is raised preferably. Like a case of R^7 , an alkyl group of R^8 may be independent and may be mixed two or more sorts.

[0098]

Although a chain of this vinyl system copolymer consists of a monomeric unit of a formula (18) and a formula (19) substantially, a "real target" here means that the sum total of a monomeric unit of a formula (18) which exists in this copolymer, and a formula (19) surpasses 50 % of the weight. The sum total of a monomeric unit of a formula (18) and a formula (19) is 70 % of the weight or more preferably.

[0099]

From a point-of compatibility with a polyoxalkylene series polymer, as for an abundance ratio of a monomeric unit of a formula (18), and a monomeric unit of a formula (19), 95.5-40:60 are preferred at a weight ratio, and 90:10-60:40 are still more preferred.

[0100]

As monomeric units other than a formula (18) which may be contained in this copolymer, and a formula (19), For example, carboxylic acid groups, such as acrylic acid and methacrylic acid, acrylamide, Amide groups, such as methacrylamide, N-methylolacrylamide, and N-methylolmethacrylamide, Epoxy groups, such as glycidyl acrylate and glycidyl methacrylate, Diethylamino ethyl acrylate, diethylamino ethyl methacrylate, A monomer containing amino groups,

such as aminoethyl vinyl ether; a monomeric unit which originates in acrylonitrile, styrene, alpha-methylstyrene, alkyl vinyl ether, VCM/PVC, vinyl propionate, vinyl acetate, vinyl propionate, ethylene, etc. in addition to this is raised.

[0101]

Although an organic polymer which blends a saturated hydrocarbon system polymer which has a reactive silicon group which has a reactive silicon group is indicated by JP.H1-168761,A, JP.2000-186176,A, etc., it is not limited to in particular these.

[0102] A method of polymerizing an acrylic ester (meta) system monomer elsewhere under existence of an organic polymer which has a reactive silicon group as a manufacturing method of an organic polymer which blends a vinyl-base polymer which has a reactive silicon group can be used. Although this manufacturing method is concretely indicated by each gazette, such as JP.59-168014,A, JP.60-228516,A, and JP.60-228517,A, it is not limited to these.

[0103] Carboxylic acid calcium used as a (B) ingredient in a hardenability constituent of this invention, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid manganese, carboxylic acid cobalt, and a carboxylic acid cobalt, such as what is called a silanol condensation catalyst in which a silicon atom contained in an organic polymer which is the (A) ingredient of this invention, or a hydrolytic basis.

[0104] In said carboxylic acid metal salt, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, and a carboxylic acid zirconium, it is more desirable from a point that the activity of a catalyst is high, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, and a carboxylic acid zirconium are still more preferred, and carboxylic acid iron and carboxylic acid titanium are especially the most preferred.

[0105] Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, it is more desirable from a point with little coloring of a hardenability constituent obtained, and a point that the heat resistance of a hardened material and weatherability which are obtained are high, and carboxylic acid calcium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, and a carboxylic acid zirconium are still more preferred.

[0106] This (B) ingredient uses as the main ingredients carboxylic acid metal salt expressed with general formula (2) – (12), respectively.

Ca(OCOR)₂ (2)

V(OCOR)₃ (3)

Fe(OCOR)₂ (4)

Fe(OCOR)₃ (5)

Ti(OCOR)₄ (6)

K(OCOR) (7)

Ba(OCOR)₂ (8)

Mn(OCOR)₂ (9)

nickel(OCOR)₂ (10)

Co(OCOR)₂ (11)

Zr(O₂OCOR)₂ (12)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)

As carboxylic acid, a carboxylic acid group content compound of a hydrocarbon system of 2-40 is used suitably, and a carbon number including carbonyl carbons may be especially used for a carboxylic acid group content compound of a hydrocarbon system of the carbon numbers 2-20 suitably from a point of availability here.

[0107]

When it illustrates concretely, acetic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, Enanthic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, Undecanoic acid, lauric acid, tridecylacid, myristic acid, pentadecyl acid, Palmitic acid, heptadecylacid, stearic acid, nonadecanoic acid, arachin acid, Behenic acid, lignoceric acid, carinic acid, montanic acid, melissic acid, Straight chain saturated fatty acid groups, such as RAKUSERU acid, Undecylenic acid, Linder acid, Tsuzuo acid, FITZETERIN acid, myristoleic acid, 2-hexadecenoic acid, 6-hexadecenoic acid, 7-hexadecenoic acid, palmitoleic acid, a petroselinic acid, Monoenoic unsaturations, such as oleic acid, elaidic acid, ASUKUREPIN acid, a gadoleic acid, Gondo Inn acid, a ceteoleic acid, erucic acid, behenic acid, stearoleic acid, KISHIMEN acid, and RUMEKUEN acid Fatty acid, Linoleic acid, 10,12-octadecadecenoic acid, HIRAGO acid, Alpha-eleostearic acid, beta-eleostearic acid, puniceic acid, linolenic acid, 8,11,14-eicosatrienoic acid, a 7,10,13-docosatrienoic acid, 4,8,11,14-hexadeca tetraenoic acid, MOROKUCHI acid, steer RIDON acid, Arachidonic acid, 8,12,16,19-docosatetraenoic acid, 4,8,12,15,18-eicosapentaenoic acid, Polyene unsaturated fatty acid, such as clupanodonic acid, docosahexaenoic acid, iso acid, Branch fatty acid, such as anteiso acid, tuberculostearic acid, a pivalic acid, and docosahexaenoic acid, A tanrio acid, Fatty acid with triple bonds, such as stear roll acid, a sterol acid, and cerebronic acid; dicarboxylic acid, such as succinic acid, glutaric acid, stearic acid, chaulmoogric acid, Chine acid; Naphthenic acid, A malvalic acid, stearoleic acid, HIDONO carbyne acid, chaulmoogric acid, Alycyclic carboxylic acids, such as genic acid; Sabinito acid, 2-hydroxytetradecanoic acid, IPURORU acid, 2-hydroxyhexadecanoic acid, YARAPI Norian acid, uni-PERIN acid, uni-AMBURETTORU acid, ARYURITTO acid, 2-hydroxyoctadecanoic acid, 12-hydroxyoctadecanoic acid, 18-hydroxyoctadecanoic acid, 9,10-dihydroxyoctadecanoic acid, Oxygenated fatty acid, such as ricinoleic acid, cam HOREN acid, licanic acid, ferroin acid, and cerebronic acid, such as succinic acid, glutaric acid, adipic acid, pinoleic acid, SUPERIN acid, azelaic acid, and sebatic acid, is mentioned.

[0108]

when the melting point of said carboxylic acid is high (crystallinity is high), the melting point becomes high in a similar manner, and it is hard to deal with carboxylic acid metal salt which has the acid radical (workability -- bad). Therefore, as for the melting point of said carboxylic acid, it is preferred that it is 65 ** or less, and it is more preferred that it is -50-50 **, and it is especially -40-35 **.

[0109]

when a carbon number of said carboxylic acid is large (a molecular weight is large), it becomes liquefied and carboxylic acid metal salt which has the acid radical becomes a thing which has a high solid state or viscosity and which is hard to deal with it (workability -- bad). On the contrary, when a carbon number of said carboxylic acid is small (a molecular weight is small), catalyst ability of carboxylic acid metal salt may fall [carboxylic acid metal salt which has the acid radical], including carboxylic acid metal salt may fall on conditions (thin layer) which mostly an ingredient which volatilizes easily with heating. Especially on conditions (thin layer) which extended a constituent thinly, volatilization by heating may be large and catalyst ability of carboxylic acid metal salt may fall greatly. Therefore, as for said carboxylic acid, it is preferred that carbon numbers including carbon of a carbonyl group are 2-17, it is more preferred that it is 3-13, and it is preferred that it is especially 5-10.

[0110]

Especially acquisition is easy, and is cheap and a point that compatibility with the (A) ingredient is good to said carboxylic acid has 2-ethylhexanoic acid, octylic acid, neo decanoic acid, oleic acid, or preferred naphthenic acid. Said naphthenic acid is expressed with an empirical formula (20). C_nH_{2n-2}O₂ (20)

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workability except that a good hardened material will become generation of heat and foaming local at the time of hardening arise, and is hard to be obtained, if loadings of the (B) ingredient exceed this

salt, 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid iron (tetravalence), 2-ethylhexanoic acid vanadium (trivalent), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid cobalt (divalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid manganese (divalent), 2-ethylhexanoic acid nickel (divalent), 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid cobalt (divalent), 2-ethylhexanoic acid zirconium (tetravalence), neo decanoic acid iron (divalent), neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), neo decanoic acid vanadium (trivalent), neo decanoic acid calcium (divalent), neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Oleic acid iron (divalent), oleic acid calcium (divalent), oleic acid vanadium (trivalent), oleic acid potassium (univalent), Oleic acid barium (divalent), manganese oleate (divalent), oleic acid nickel (divalent), Oleic acid cobalt (divalent), an oleic acid zirconium (tetravalence), naphthenic acid iron (divalent), Naphthenic acid iron (trivalent), naphthenic acid titanium (tetravalence), naphthenic acid vanadium (trivalent), manganese naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), manganese naphthenate (divalent), naphthenic acid nickel (divalent), cobalt naphthenate (divalent), a naphthenic acid zirconium (tetravalence), etc. are mentioned.

[0112] 2-ethylhexanoic acid iron (divalent) from a viewpoint of catalytic activity, 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid titanium (tetravalence), neo decanoic acid iron (divalent), Neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), oleic acid iron (divalent), Oleic acid iron (trivalent), oleic acid titanium (tetravalence), naphthenic acid iron (divalent), Naphthenic acid iron (trivalent) and naphthenic acid titanium (tetravalence) are more preferred, and 2-ethylhexanoic acid iron (trivalent), neo decanoic acid iron (trivalent), oleic acid iron (trivalent), and naphthenic acid iron (trivalent) are preferred.

[0113] From a viewpoint of coloring to 2-ethylhexanoic acid titanium (tetravalence), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid zirconium (tetravalence), Neo decanoic acid titanium (tetravalence), neo decanoic acid calcium (divalent), Neo decanoic acid potassium (univalent), Neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Oleic acid titanium (tetravalence), oleic acid calcium (divalent), oleic acid potassium (univalent), Oleic acid barium (divalent), an oleic acid zirconium (tetravalence), naphthenic acid titanium (tetravalence), calcium naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid zirconium (tetravalence) are more preferred.

[0114] Such carboxylic acid metal salt makes a carboxylic acid group content compound, or its ester and sodium hydroxide react, and makes solution of hard soap. Solution of metal salt prepared apart from this In addition, a sedimentation method which settles metallic soap. A carboxylic acid group content compound or its ester and melted hydroxide, an oxide, A method etc. to which an alcoholate or a chloride, and a carboxylic acid group content compound are made to react in [else /, such as siccification to which a weak acid salt is made to react at an elevated temperature, and direct method to which a carboxylic acid group content compound and metal powder are made to react,] an anhydrous organic solvent are taken.

[0115] As for such carboxylic acid metal salt, it is preferred to dilute with diluting solvents, such as a mineral spirit, toluene, hexylene glycol, a diethylene glycol, a paraffin oil, and dioctyl phthalate, and to be used with a gestalt of a solution whose metal content is about 1 to 40 % of the weight.
[0116]

(B) About 0.005-5 weight sections are preferred at metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as amount of ingredient used, and also about 0.01-3 weight sections are preferred. (B) Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings of an ingredient are less than this range, it is not desirable. On the other hand, pot life becomes short too much and is not preferred from a point of

workability except that a good hardened material will become generation of heat and foaming local at the time of hardening arise, and is hard to be obtained, if loadings of the (B) ingredient exceed this

The aforementioned carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. Besides using it alone, it can be used combining two or more sorts, and also can use together with carboxylic acid tin salt, carboxylic acid lead salt, carboxylic acid bismuth salt, carboxylic acid ceric salt, etc. [0117]

[0118] On the other hand, only with carboxylic acid metal salt of the (B) ingredient, activity is low, and when moderate hardenability is not acquired, various amine compounds which are the (C) ingredients as a co-catalyst can be added. As various amine compounds, although indicated to JP H5-28187 A, for example, Specifically Methylamine, ethylamine, propylamine, isopropylamine, A butylamine, amyl amine, hexylamine, octylamine, 2-ethylhexylamine, Nonyl amine, decyl amine, lauryl amine, pentadecyl amine, Aliphatic series primary amines, such as Sept Iles amine, stearylamine, and cyclohexylamine; Dimethylamine, Diethylamine, dipropyl amine, diisopropylamine, dibutyl amine, diamylamine, diocetyl amine, di(2-ethylhexyl) amine, didecyl amine, dilauryl

Amine, JISECHRU amine, diisocetylamine, methylstearylamine, Aliphatic series secondary amines, such as ethylstearylamine and butylstearylamine; Triethylamine, Aliphatic series tertiary amines, such as triamylamine, trihexyl amine, and trioctylamine; Triaryl amine, Aliphatic series unsaturation amines, such as oleylamine; Lauryl amine, As aromatic amine [such as stearylamine], a triphenylamine N-N-dimethylamine, and dimethylbenzyl aniline,]; and other amines. Monoethanolamine, diethanolamine, triethanolamine, Dimethylamino ethanol, diethylenetriamine, triethylenetetramine, Tetraethylenepentamine, benzylamine, diethylamino propylamine, Xylylene diamine, ethylenediamine, hexamethylenediamine, Dodecamethylene diamine, dimethylethylene diamine, triethylendiamine, Guanidine, diphenylguanidine, N,N,N', and N'-tetramethyl 1,3-butenediamine, N,N,N', N'-tetramethyl ethylene diamine, 2,4,6-tris(dimethyl aminomethyl) phenol, Although morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene 7 (DBU) etc. are mentioned, it is not limited to these.

[0119] In this invention, an amino group content silane coupling agent can also be used as a (C) ingredient. Said amino group content silane coupling agent is a compound which has a basis (henceforth a hydrolytic silicon group) and an amino group containing a silicon atom which a hydrolytic basis combined. As an example of this hydrolytic silicon group X can mention a thing which is a hydrolytic basis among bases expressed with a general formula (1). Although a basis already illustrated as a hydrolytic basis can specifically be mentioned, a methoxy group, an ethoxy group, etc. are preferred from a point of a hydrolysis rate. As for especially the two or more number of a hydrolytic basis, three or more bases are preferred.

gamma-2-aminoethyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, N-vinylbenzyl gamma-aminopropyl triethoxysilane, etc. can be mentioned. Amino modifying sily polymer which is the denatured derivative, silanizing amino polymer, an unsaturation aminosilane complex, a phenylamino long chain alkyl silane, amino silanizing silicone, etc. can use these. The above-mentioned amino group content silane coupling agent may be used only by one kind, and may carry

[0121] As these (C) ingredients, since co-catalyst ability changes greatly with structure of the (C) ingredient itself, compatibility with the (A) ingredient, etc., it is preferred to choose a compound which was out two or more kind mixing use.

suitable according to a kind of (A) ingredient to be used. For example, when using an isobutylene system polymer as a (A) ingredient, aliphatic series secondary amines, such as comparatively long-chain aliphatic series secondary amines, such as diethyl amine and diisopropyl amine, and dicyclohexylamine, are preferred from a point that co-catalyst ability is high.

[0122]

As for loadings of an amine compound which is the aforementioned (G) ingredient, about 0.01–20 weight sections are preferred to organic polymer 100 weight section of the (A) ingredient, and also 0.1–5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much and is not preferred from a point of workability.

[0123]

Silane coupling agents other than an amino group content silane coupling agent can also be used for a constituent of this invention.

[0124] As functional groups other than an amino group, a sulphydryl group, an epoxy group, a carboxyl group, a vinyl group, an isocyanate group, isocyanurate, halogen, etc. can be illustrated.

[0125] As an example of silane coupling agents other than an amino group content silane coupling agent, gamma-mercaptopropyltrimethoxysilane, gamma-mercaptopropyl triethoxysilane, Sulphydryl group content Silang, such as gamma-mercaptopropylmethyl dimethoxysilane and gamma-mercaptopropylmethyl diethoxysilane; Gamma-glycidoxypyropyltrimetoxysilane, gamma-glycidoxypyropyltrimethoxysilane, gamma-glycidoxypyropylmethylmethoxysilane, beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypyropylmethylmethoxysilane, such as beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane; beta-carboxyethyl triethoxysilane, beta-carboxyethyl phenylbis(2-methoxyethoxy)Silang. Carboxylsilanes, such as N-heta-(carboxymethyl) aminoethyl gamma-aminopropyl trimethoxysilane; Vinyltrimetoxysilane, vinyltrimethoxysilane, gamma-methacryloyloxypropyl methyl dimethoxysilane, vinyl type unsaturation group content Silang [such as gamma-oxypropyl methyl trimethoxysilane, vinyl propylmethyl trimethoxysilane,], — containing halogen Silang [such as gamma-ALKURO yloxy propylmethyl trimethoxysilane,], — isocyanurate silanes [such as tris (trimethylsilyl) isocyanurate,], Isocyanate group content Silang, such as gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propyl trimethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, and gamma-isocyanate propylmethyl dimethoxysilane, can be mentioned. A block isocyanate silane, silanizing polyester, etc. which are the derivatives which denaturalized these can be used as a silane coupling

[0126] The amount of [in case used of using silane coupling agents other than an amino group content silane coupling agent] has 0.01 - 20 preferred weight section to (A) ingredient 100 weight section, agent.

[0127] Various fillers can be used for a hardenability constituent of this invention if needed. As an example of said filler, for example Wood flour, PARUBU, a cotton chip, Asbestos, glass fiber, carbon fiber, mica, walnut shell powder, chaff powder, Graphite, diatomite, clay, fume silica, sedimentation nature silica, Crystalline silica, fused silica, dolomite, a silicic acid anhydride, carbon black, calcium carbonate, clay, talc, titanium oxide, aluminium hydroxide, magnesium carbonate, aluminum impalpable powder, the Flint powder, the end of zinc dust, etc. are raised. Among these fillers, sedimentation nature silica, fused silica, crystalline silica, fused silica, dolomite, carbon black, calcium carbonate, titanium oxide, talc, etc. are more preferred than others, such as a reinforcing effect, the increase in quantity effect, and an ease of acquisition. These fillers may be used independently and may be used together two or more sorts. The amount of [in case used of using a filler] has 10 - 1000 preferred weight section to (A) ingredient 100 weight section; and its 50 ~ 300 weight section is still more and also its U. - 3 weight section is more preferred.

[0128] In a hardenability constituent of this invention, since elongation of a hardened material can be preferred.

bulking agent, it is more effective. As an example of a plasticizer, diethyl phthalate, dibutyl phthalate, di-*iso*octyl phthalate, and JIS O undeoyl phthalate; Diethyl adipate, *** aliphatic dibasic acid ester, such as succinic acid isodecyl and dicapric acid ester, such as pentadecyl tritoly ester; Butyl ole sebacate; Diethylene glycol dibenzoate, *** glycol ester, such as pentadecyl tritoly ester; Tricresyl phosphite, *** aliphatic series ester, such as methyl acetyl ricinoleate; Tricresyl phosphite; Epoxidized soybean phosphoric ester, such as trioctyl phosphite and phosphoric acid octylidiphenyl; Polyethyl oil, *** epoxy plasticizers, such as epoxidation linseed oil and epoxy stearic acid benzyl; Polyethyl such as a polyester plasticizer; polypropylene glycol which is polyester of dibasic acid and dihydroxy alcohol, and its derivative; [Poly alpha-methylstyrene.] Polystyrene, such as polystyrene; Polybutadiene, Butadiene Acrylonitrile, polychloroprene, polyisoprene, polybutene, hydrogenation polybutadiene, hydrogenation polyisoprene, Hydrocarbon system oligomer, such as process oil; chlorinated paraffins are illustrated

[0129] These plasticizers may be used alone and may be used together two or more sorts. A desirable result will be obtained if the amount of plasticizers is used in the range of one to 200 weight section to reactive-silicon-group-containing-organic-polymer 100 weight section.

[0130] An epoxy resin can be used together in a hardenability constituent of this invention. In this case, an epoxy resin and reactive silicon group containing organic polymer can be reformed.

[0131] As an epoxy resin, can use a publicly known thing widely conventionally, and For example, a bisphenol A type epoxy resin, Fire retardancy type epoxy resins, such as bisphenol F type epoxy resin and glycidyl ether of tetrabromobisphenol A, Novolak type epoxy resin, a hydrogenation bisphenol A type epoxy resin, A glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, Diglycidyl p-oxibenzoic acid phthalic acid diglycidyl ester, Phthalic acid diglycidyl ester system epoxy resins, such as tetrahydrophthalic acid diglycidyl ester and diglycidyl hexahydrophthalate, m-aminophenol series epoxy resin, a diaminodiphenylmethane system epoxy resin, Urethane modified epoxy resin, various cycloaliphatic-epoxy-resin, N, and N-diglycidyl aniline, N,N-diglycidyl o-toluidine, triglycidyl isocyanurate, An unsaturation thing of unsaturation polymers, such as glycidyl ether of polyhydric alcohol, such as polyalkylene glycol diglycidyl ether and glycerin, a hydantoin type epoxy resin, and

[0132] It is desirable from a point of a thing containing at least two epoxy groups having high reactivity when hardening, and a hardened material tending to form the three-dimensional network structure into a molecule, also in these epoxy resins. As a desirable epoxy resin, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, novolak type epoxy resin, and a phthalic acid diglycidyl ester system (urethane resin), etc., can be mentioned.

[0133] As a hardening agent of an epoxy resin, a publicly known hardening agent for epoxy resins can be used widely conventionally. For example, triethylenetetramine, tetraethylenepentamine, diethylamino propylamine, N-aminooethyl piperazine, m-xylylene diamine, m-phenylenediamine, Diaminodiphenylmethane, diaminodiphenyl sulfone, isophoronediamine, amines, such as 2,4,6-tris (dimethyl aminomethyl) phenol, Tertiary amine salts, polyamide resin, ketimines, and aldimine. Insidiumethyl hardening agents, such as enamines, imidazole derivatives, and dicyandiamides. Boron trifluoride complex compounds, phthalic anhydride, hexahydro phthalic anhydride, Anhydrous carboxylic acid, such as tetrahydro phthalic anhydride and methylene tetrahydro phthalic anhydride, a DODESHINIRU succinic anhydride, pyromellitic dianhydride, and anhydrous KUROREN acid, alcohols,

An epoxy resin receives reactive-silicon-group-containing-organic-polymer 100 weight section. It is preferred to use it in the range of one to 100 weight section and also ten to 50 weight section, and it is preferred to blend a hardener amount of an epoxy resin or epoxy resin 100 weight section in the phenols, and carboxylic acid can be mentioned.

An ingredient which limitation in particular does not have in the method of preparation of a resin preferred to diene a hardening agent or an epoxy resin per cent to weight percent range of one to 200 weight section and also ten to 100 weight section. [0135]

hardenability constituent of this invention, for example, was described above is blended, it kneads under ordinary temperature or heating using a mixer, a roll, a kneader, etc., or an ingredient is dissolved using a little suitable solvents, and a usual method of mixing may be adopted. A 1 liquid type, two-component type, or many liquid type compound can also be built and used by combining these ingredients suitably.

[0136] If a Hardenability constituent of this invention is exposed into the atmosphere, by operation of moisture, it will form network structure in three dimensions, and will harden it to a solid which has rubber-like elasticity.

[0137] In a Hardenability constituent of this invention, various additive agents can be added if needed. Other curing catalysts as an example of said additive for example (for example, tetravalent tin, divalent tin, etc.). Adhesive graft agents which adjust the tractive characteristics of a hardened material to generate, such as a physical-properties regulator and a silane coupling agent. An antioxidant, radical inhibitor, an ultraviolet ray absorbent, a metal deactivator, anti-ozone, light stabilizer, the Lynn system peroxide decomposition agent, lubricant, paints, a foaming agent, a photo-setting resin, and thixotropic graft agent, etc. are raised.

[0138] An example of such an additive is indicated in each gazette of JP 4-69659,B, JP,7-108928,B, JP,63-254149,A, and JP,64-22804,A, for example.

[0139] Since a Hardenability constituent of this invention has outstanding weatherability, heat resistance, water resisting property, and electric insulation resulting from a principal chain skeleton and it has high intensity and a physical-properties improvement effect of high elongation. It can use conveniently for electrical insulation materials, such as electric electronic component materials, such as a structural elastic sealing compound, a sealing material for multiple glass, a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, a binder, adhesives, a paint, infusion, a coating material, a sealing agent for rust prevention / water proof, etc. It is useful especially when used for adhesives, a structural elastic sealing compound, or a sealing material for siding.

[0140] Although working example and a comparative example explain this invention concretely below, this invention is not limited to this.

[0141] (Working example 1-4, comparative example 1)

(A) As opposed to isobutylene system polymer (Kanska Corp. make, trade name EP505S;isobutylene system polymer / paraffin series process oil = 100/50) 150 weight section which has a reactive silicon group as an ingredient, Epoxy resin (product [made from Oil recovery Shell Epoxy], trade name Epicot 828) 5 weight section, Hydrogenation alpha-olefin oligomer (product [made from Idemitsu Petrochemistry], trade name PA0504) 60 weight section, Colloid calcium carbonate (Maru Calcium Co., Ltd. make, trade name SHIRETTSU 200) 50 weight section, Colloid calcium carbonate (Maru Calcium Co., Ltd. make, trade name MG-5) 50 weight section, Heavy-calcium-carbonate (product [made from Shiroishi Calcium], trade name SOTNIKKUSU M-309) 3 weight section, Photo-setting resin (Toagosei make, trade name ARONIKKUSU M-309) 3 weight section, Benzo triazol system ultraviolet ray absorber (Giba-Geigy Japan make, trade name tinuvin 327) 1 weight section, hindered amine light stabiliser (Sankyo Co., Ltd. make, trade name SANORU LS-770) 1 weight section, hindered phenolic antioxidant (Giba-Geigy Japan make, trade name IRUGA NOx 1010) 1 weight section, and water 5 weight section were measured respectively, and it often kneaded with a 3 paint roll, and was considered as base resin.

[0142] next — as the (B) ingredient — octylic acid (2-ethylhexanoic acid) calcium salt (the Nihon Kagaku Sangyo Co., Ltd. make.) The trade name NIKKANAFU textile V 2% toluene solution and the (C) ingredient — distearyl amine (the Kao Corp. make.) The number[of weight sections]-used thing which shows Firm D86 in Table 1 respectively is made into working example 2, (B), as an ingredient — octylic acid (2-ethylhexanoic acid) iron (the Nihon Kagaku Sangyo Co., Ltd. make.) The number[of weight sections]-used thing which shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a trade name NIKKAOOKU Chicks Fe 6% toluene solution and a (C) ingredient is made into working example 3, The number[of weight sections]-used thing which furthermore shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a (B) ingredient as octylic acid (2-ethylhexanoic acid) titanium (3% toluene solution) and a (C) ingredient was made into working example 4. On the other hand, the number[of weight sections]-used thing which shows lauryl amine in Table 1 respectively as (B) octylic acid (2-ethylhexanoic acid) tin (Japanese east transformation Make, trade name neo SUTAN U-28) and a (C) ingredient was made into the comparative example 1.

[0143] These base resin and hardening agents were mixed by the ratio shown in Table 1, respectively, and what constructed the aluminum base material to H type in accordance with the manufacturing method of the tensile adhesive property specimen to which this is specified JIS A5758-1992 was filed up. Care-of-heath conditions were made into 23 ***x 7 +50 ***x seven days, [per day] The used aluminum uses the alumite treatment aluminum of the 50x50x5-mm size based on JIS H4000 as a substrate. After purifying by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.) before being filled up with the compound, the primer (the Toray Industries Dow Corning make, trade name D-2) was dried and used under ordinary temperature for spreading and 30 minutes.

[0144] In accordance with the tensile cement test method of 5758 - 1992 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method on condition of speed-of-testing 50 mm/min among 23 *** and the thermosstatic chamber of 50***5% of humidity.

[0145] The recovery was measured by the following methods. First, after making H type sample which ended the above-mentioned care of health immersed into 50 ** warm water for one day and taking it out, it was neglected under the room temperature on the 1st. Subsequently, after having compressed and fixed to 70% so that sample thickness might be set to 12 to 8.4 mm, and heating a sample in 100 ** hot air drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of the sample in this case was measured and the recovery to a compressed part was computed.

[0146] The recovery was measured by the following methods. First, after making H type sample which ended the above-mentioned care of health immersed into 50 ** warm water for one day and taking it out, it was neglected under the room temperature on the 1st. Subsequently, after having compressed and fixed to 70% so that sample thickness might be set to 12 to 8.4 mm, and heating a sample in 100 ** hot air drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of the sample in this case was measured and the recovery to a compressed part was computed.

[0147] Time (leather-covered time) until it fills the same compound in an ointment can simultaneously as a measure which estimates hardenability and stretches a hide on the surface under 23 ** and the conditions of 50% of relative humidity was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0148] A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

[0143]

here — as the (B) ingredient of this invention — naphthenic acid vanadium (the Nihon Kagaku Sangyo Co., Ltd. make.) as a trade name NIKKANAFU textile V 2% toluene solution and the (C) ingredient — distearyl amine (the Kao Corp. make.) The number[of weight sections]-used thing which shows Firm D86 in Table 1 respectively is made into working example 2, (B), as an ingredient — octylic acid (2-ethylhexanoic acid) iron (the Nihon Kagaku Sangyo Co., Ltd. make.) The number[of weight sections]-used thing which shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a trade name NIKKAOOKU Chicks Fe 6% toluene solution and a (C) ingredient is made into working example 3, The number[of weight sections]-used thing which furthermore shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a (B) ingredient as octylic acid (2-ethylhexanoic acid) titanium (3% toluene solution) and a (C) ingredient was made into working example 4. On the other hand, the number[of weight sections]-used thing which shows lauryl amine in Table 1 respectively as (B) octylic acid (2-ethylhexanoic acid) tin (Japanese east transformation Make, trade name neo SUTAN U-28) and a (C) ingredient was made into the comparative example 1.

[0144]

These base resin and hardening agents were mixed by the ratio shown in Table 1, respectively, and what constructed the aluminum base material to H type in accordance with the manufacturing method of the tensile adhesive property specimen to which this is specified JIS A5758-1992 was filed up. Care-of-heath conditions were made into 23 ***x 7 +50 ***x seven days, [per day] The used aluminum uses the alumite treatment aluminum of the 50x50x5-mm size based on JIS H4000 as a substrate. After purifying by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.) before being filled up with the compound, the primer (the Toray Industries Dow Corning make, trade name D-2) was dried and used under ordinary temperature for spreading and 30 minutes.

[0145]

In accordance with the tensile cement test method of 5758 - 1992 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method on condition of speed-of-testing 50 mm/min among 23 *** and the thermosstatic chamber of 50***5% of humidity.

[0146]

The recovery was measured by the following methods. First, after making H type sample which ended the above-mentioned care of health immersed into 50 ** warm water for one day and taking it out, it was neglected under the room temperature on the 1st. Subsequently, after having compressed and fixed to 70% so that sample thickness might be set to 12 to 8.4 mm, and heating a sample in 100 ** hot air drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of the sample in this case was measured and the recovery to a compressed part was computed.

[0147]

Time (leather-covered time) until it fills the same compound in an ointment can simultaneously as a measure which estimates hardenability and stretches a hide on the surface under 23 ** and the conditions of 50% of relative humidity was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0148]

A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

[0149]

[Table 1]

[0150] Using an isobutylene system polymer as an ingredient (A) as shown in Table 1 as a (B) ingredient, when diisobutyl amine and lauryl amine were used together for octylic acid calcium, naphthenic acid varnadium, and octylic acid titanium as a co-catalyst (working example 1, 2, and 4), the leather-covered time about equivalent has been secured as compared with the case where octylic acid tin and lauryl amine of the comparative example 1 are used together. On the other hand, in the case (working example 3) where used octylic acid iron as a (B) ingredient, and lauryl amine used as a catalyst, although it had been 9 hours or more leather-covered time, one day afterward, it checked having hardened enough. The hardened material which was obtained also in the gap to use such carboxylic acid metal salt for (working example 1-4) showed breaking strength with high all, and elongation after fracture to the comparative example 1 which used octylic acid tin and lauryl amine. About stability, although the recovery at the time of using octylic acid titanium and octylic acid iron was lower than the comparative example 1, all had stability. High stability was shown when especially the leather-covered time was used (working example 2).

[0151] [\[View\]](#) [\[Edit\]](#) [\[Delete\]](#)

(Working example 5, comparative example 2)
 (A) As a polyether system polymer which has polymer S203 (made by Kaneka Corp.) 95 weight section and a dripping inhibitor (made DISUPARON #6500 duplex, benzotriazol sys trade name tinuvin 327) 1 weight section, and trade name SANORU LS-7010 1 weight section calcium carbonate (the product made from stirring at 120 ** with 5L planetary mixer before CCR120 weight section and titanium oxide (R-820) 20 weight section, and stirring mixing and it kneaded once with 3 paint roll, and also for 2 hours, and water content decreased to cooling a mixture, it added and stirring mixing trade name A-171) duplex was carried out from aminosilane coupling agent (Nippon Unicar made out for 15 minutes. The octylic acid zirconium (C) The number of weight sections which were ingredient in Table 2, and the mixed thing were

performed for 5 minutes. The cartridge made of paper (product made from the Showa round cylinder) by which the coat was carried out was filled up with the aluminum for 1 liquid so that the obtained mixture might not involve in a bubble, and 1 liquid mold-curing nature constituent was obtained. What used the amount part of diisobutyl diacetyl acetonate (Japanese east transformation Make, trade names U-220) duplexes was made into the comparative example 2 instead of the mixture of said isobutyl acid dicoumarin and lauroyl amine.

[0152] After neglecting the above-mentioned 1 liquid mold-curing nature constituent under a room temperature for 24 hours or more, the specimen used for a tensile test was produced as follows. What constructed the aluminum base material to H1 type in accordance with the manufacturing method of the tensile adhesive property specimen specified to JIS A5758-1992 using the cancer of marketing of 1 liquid mold-curing nature constituent from 1 liquid cartridge was filled up. Care of-
heat conditions were made into 23 **x1.4 +50 **x 14 days. [per day] Using the alumite treatment aluminum of the 50x50x5-mm size based on JIS H44000 before the aluminum used as a substrate was filled up with the compound, it was purified by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.). In accordance with the tensile cement test method of 5758 - 1992 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method on condition of for 23 **, and humidity 50 inside of +5% of thermostatic chamber and speed-of-testing [of 50 mm]. The hardened material set stress when it elongated 150% to M50, M100, and M150 100% 50%, respectively, and set TB and elongation at the time of a fracture to EB for the stress at

[0153] Since an adhesive property turned into the important characteristic as a liquid mold-curing nature constituent, the adhesive property was checked using anodized aluminum and a vinyl chloride steel plate. On each substrate which purified the surface by methyl ethyl ketone, 1 liquid mold-curing nature constituent was placed from 1 liquid cartridge using commercial cancer to the crest shape with a 1 cm² in width] x length of about 3 cm, and it was recuperated for 23 ***x14+50** x 14 days per day. The manual friction test was done after care of health, cutting an adhesion side deeply with a cutter knife, and the surface of the substrate was observed. The filled hardened material is that cohesive failure is shown, and GF in Table 2 is a fracture state searched for as a sealing material.

[0154] Depths hardenability took out the portion which has hardened the surface which filled in the 80-mm-long polyethylene tube 1 liquid mold-curing nature constituent produced in working example 5, and was made at the tip of a tube in it at 16.5 mm in inside diameter, on the day which the days to

measure visited, and measured the hardened thickness with slide calipers.

[1055] In order to check the practicality as a 1 liquid mold-curing nature constituent, where 1 liquid cartridge is filled up with a constituent, it stored for two weeks in the hot air drying equipment which carried out the temperature control to 50 **, and the depths hardenability after storage was investigated. A result is shown in Table 2.

[0156]
[Tahs 3]

試験名	試験名	結果	結果
(A) 実験	MS名	溶融	溶融
可燃性	S203	95	直燃
PG3000	S20	95	直燃
燃焼ガスCCR	120	120	直燃
燃焼性試験	サードレバ-770	1	直燃
毒性試験	チルビン-287	1	直燃
生物活性試験	エフエス-462-4670	2	直燃
生物活性試験	エフエス-28-850	20	直燃
生物活性試験	A-171	2	直燃
生物活性試験	A-1120	3	直燃
(B) 混合	オクタデシルジメチルシリコン	8.1	直燃
	U-220	2	直燃
(C) 混合	テルルメチル	1.4	直燃
	M150	0.19	MPa
	M150	0.38	MPa
	M150	0.46	MPa
	M150	0.93	MPa
溶解性	溶融化アルミニウム	520	CF
		CF	吸湿性
溶解性	溶融化性	23℃±1時間	10.6 mm
		23℃±2時間	15.6 mm
溶解性	溶融化性	23℃±1時間	10.8 mm
(SDC×2時間計量)		23℃±2時間	16.4 mm

[0157]

As opposed to the polyether system polymer which serves as the (A) ingredient of this invention in working example 5, (B) By using the lauryl amine which acts the carboxylic acid zirconium salt which acts as a co-catalyst as a (C) ingredient further as a silanol condensation catalyst as an ingredient, Although hardenability was slightly inferior as compared with the comparative example 2 using dibutyltin diacetyl acetone as a tetravalent tin catalyst, almost comparable elongation and an adhesive property were revealed and it checked that 1 liquid mold-curing nature constituent which may be sufficient for practical use was obtained (Table 2).

[0158]

(Synthetic example 1) Use polyoxypropylene triol of the molecular weight 3,000 [about] as an initiator, and propylene oxide is polymerized in a zinc hexa cyanocobaltate glyme complex compound catalyst. Number average molecular weight about 26,000 (polystyrene reduced molecular weight in which the column measured the solvent using THF using the TOSOH TSK-GEL H type using TOSOH HLC-8120GPC as a liquid-sending system) polypropylene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent was added 1.2 times to the hydroxyl group end polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxylation reaction was performed. end was changed into the allyl group. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about] which is an allyl group.

[0159]

The nitrogen purge was carried out, after having added 500 g of allyl end 3 organic-functions polypropylene oxide and 10 g of hexane which were obtained above to 1L autoclave, dehydrating azeotropically at 90 ** and distilling off hexane under decompression. On the other hand, after adding 30ml of platinum divinyldisiloxane complex (it is 3% of the weight of xylene solution by platinum conversion) 1.7.0 g of dimethylmethoxymethylsilane was dropped. After making the mixed solution react at 90 ** for 2 hours, unreacted dimethylmethoxymethylsilane was distilled off under decompression and the reactive silicon group content polyoxyalkylene series polymer (A-1) was obtained. The number average molecular weight of the obtained polymer (A-1) was about 26,000. The silyl group introduction rate was measured by the following methods by $^1\text{H-NMR}$ (it measures in a CDCl_3 solvent using JEOL JNM-LA400).

[0160]

. Receive the peak integral value of CH_3 group (near 1.2 ppm) of the polypropylene oxide main chain of said allyl end 3 organic-functions polypropylene oxide before a hydroxylation reaction. Relative value of the peak integral value of an allyl end proton (near $\text{CH}_2=\text{CH}-\text{CH}_2$ -5.1 ppm) : <1>. Receive the peak integral value of CH_3 group (near 1.2 ppm) of the polypropylene oxide main chain of the silyl

end polypropylene oxide (A-1) after a hydroxylation reaction. Relative-value: <2> of the peak integral value of the proton (near $\text{CH}_3(\text{CH}_3\text{O})_2\text{Si}-\text{CH}_2-\text{CH}_2$ -0.6 ppm) of the methylene group combined with the silicon atom of the end silyl group to the silyl group introduction rate (<2>/<1>) was 78%.

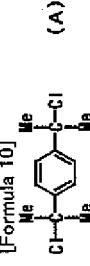
[0161]

(Synthetic example 2)

After attaching a three-way cock to the resisting pressure glass container of 2L and carrying out the nitrogen purge of the inside of a container to it. Using an injector, in a container 262.5 ml of ethylcyclohexane (thing dry by neglecting 1 or more night with the molecular sieves 3A), and 787.5 ml of toluene (thing dry by neglecting 1 or more night with the molecular sieves 3A), p-DCC (the following compound (A)) 4.85g (21.0mmol) was added.

[0162]

[Formula 10]



[0163] Next, the resisting pressure glass liquefied gas extraction pipe with a needle valve containing 438 ml (5.15 mol) of isobutylene monomers was connected to the three-way cock, and after attaching the polymerization vessel all over dry ice / ethanol bus of -70 ** and cooling, the inside of a container was made decompression using the vacuum pump. After opening the needle valve and introducing an isobutylene monomer in a polymerization vessel from a liquefied gas extraction pipe, the inside of a container was returned to ordinary pressure by introducing nitrogen from one side in a three-way cock. Next, 0.72 g (7.7mmol) of 2-methylpyridine was added. Next, 10.58 ml (96.5mmol) of titanium tetrachloride was added, and the polymerization was started. 70 minutes after the polymerization start, 7.20 g (63.0mmol) of allyl trimethylsilane was added, and the introduction reaction of the allyl group was performed to molecular chain terminals. After adding allyl trimethylsilane and 200 ml of water washed [120 minutes] the reaction solution 4 times, the allyl end isobutylene system polymer was obtained by distilling off a solvent.

[0164]

Subsequently, the allyl end isobutylene system polymer 200g obtained in this way, the paraffin-base process oil (the Idemitsu Kosan make.) which is a hydrocarbon system plasticizer After mixing trade name Diana process PS-32 100g and carrying out temperature up to about 75 **, the 7.5x10⁻⁵ equivalent was added [methyl dimethoxysilane] for 2.4 Eq and a platinum (vinyl siloxane) complex to the allyl group of an end to the allyl group of an end, and the hydrosilylation reaction was performed. FT-IR (Shimadzu IR-408) performed reaction pursuit, and the absorption based on the olefin of 1640 cm^{-1} disappeared in about 20 hours.

[0165]

2/1 of PS-32 which is the isobutylene system polymer and plasticizer which have a reactive silicon group in the both ends of the target chain of the mixtures (A-2) of the weight ratio were obtained. In this way, if the obtained polymer is measured by the GPC method (it was considered as the liquid-sending system and, as for the solvent, the column used CHCl_3 using Shodex K-804 using LC Module1 made from Waters). The number average molecular weight was 17,600 and Mw/Mn (ratio of weight average molecular weight to a number average molecular weight) was 1.23. $^1\text{H-NMR}$ (using Varian Gemini300) (The proton which belongs to each structure by measurement in CDCl_3 (the proton origin of initiator origin: 6.5-7.5 ppm) The methyl proton combined with the silicon atom of polymer-terminal origin: As a result of measuring and measuring the intensity of 0.0-0.1 ppm and the resonance signal of methoxy proton: 3.4 - 3.5, the end silyl functional group number Fn (number of the silyl group per one molecule of isobutylene polymer) was 1.76.

[0167]

(Working example 6-15, comparative example 3)

(A) As an ingredient, various additive agents were measured, respectively, and it often kneaded with a

3 paint roll according to the formula shown in Table 2, using the reactive silicon group content polyoxyalkylene series polymer (A-1) obtained in the synthetic example 1, and was considered as base resin.

[0068] Next, as a (B) ingredient which is a silanol condensation catalyst, lauryl amine was further measured for the various carboxylic acid metal salt shown in Table 1 to the above-mentioned base resin as a (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for all the numbers of mol% of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0169] The mold about 3 mm thick was used and filled up with the spatula after mixing, and care of health on 23 ***x 3 +50 #px the 4th was performed. [per day] From the obtained hardened material sheet, the No. 3 type dumbbell specimen specified to JIS K 6301 was pierced, and the tensile test was carried out in the autograph (tension speed 200 mm/min). The modulus (M5G) in the time of being extended 50%, the tensile stress at the time of a dumbbell fracture (Tb), and the elongation at the time of a dumbbell fracture (Eb) were measured.

[0170] The combination presentation of base resin, a curing catalyst, etc. and the physical-properties obtained from it are shown in Table 3

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[0172]

When the various carboxylic acid metal salt of

comparative example 3 using 2-ethylhexanoic acid.

Table 3. the value of Tb (breaking strength) and

Physical properties is larger.

High elongation and high intensity were shown.

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http://www.industryministry.gov.in/4mon-web.cgi?file?path=...&http%3A%2F%2Fwww4.ind... 2010/05/06

2010/05/01

Table 4		Comparative example 4									
1	2	3	4	5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20	21	22	23	24
25	26	27	28	29	30	31	32	33	34	35	36
37	38	39	40	41	42	43	44	45	46	47	48
49	50	51	52	53	54	55	56	57	58	59	60
61	62	63	64	65	66	67	68	69	70	71	72
73	74	75	76	77	78	79	80	81	82	83	84
85	86	87	88	89	90	91	92	93	94	95	96
97	98	99	100	101	102	103	104	105	106	107	108
109	110	111	112	113	114	115	116	117	118	119	120
121	122	123	124	125	126	127	128	129	130	131	132
133	134	135	136	137	138	139	140	141	142	143	144
145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168
169	170	171	172	173	174	175	176	177	178	179	180
181	182	183	184	185	186	187	188	189	190	191	192
193	194	195	196	197	198	199	200	201	202	203	204
205	206	207	208	209	210	211	212	213	214	215	216
217	218	219	220	221	222	223	224	225	226	227	228
229	230	231	232	233	234	235	236	237	238	239	240
241	242	243	244	245	246	247	248	249	250	251	252
253	254	255	256	257	258	259	260	261	262	263	264
265	266	267	268	269	270	271	272	273	274	275	276
277	278	279	280	281	282	283	284	285	286	287	288
289	290	291	292	293	294	295	296	297	298	299	300
301	302	303	304	305	306	307	308	309	310	311	312
313	314	315	316	317	318	319	320	321	322	323	324
325	326	327	328	329	330	331	332	333	334	335	336
337	338	339	340	341	342	343	344	345	346	347	348
349	350	351	352	353	354	355	356	357	358	359	360
361	362	363	364	365	366	367	368	369	370	371	372
373	374	375	376	377	378	379	380	381	382	383	384
385	386	387	388	389	390	391	392	393	394	395	396
397	398	399	400	401	402	403	404	405	406	407	408
409	410	411	412	413	414	415	416	417	418	419	420
421	422	423	424	425	426	427	428	429	430	431	432
433	434	435	436	437	438	439	440	441	442	443	444
445	446	447	448	449	450	451	452	453	454	455	456
457	458	459	460	461	462	463	464	465	466	467	468
469	470	471	472	473	474	475	476	477	478	479	480
481	482	483	484	485	486	487	488	489	490	491	492
493	494	495	496	497	498	499	500	501	502	503	504
505	506	507	508	509	510	511	512	513	514	515	516
517	518	519	520	521	522	523	524	525	526	527	528
529	530	531	532	533	534	535	536	537	538	539	540
541	542	543	544	545	546	547	548	549	550	551	552
553	554	555	556	557	558	559	560	561	562	563	564
565	566	567	568	569	570	571	572	573	574	575	576
577	578	579	580	581	582	583	584	585	586	587	588
589	590	591	592	593	594	595	596	597	598	599	600
601	602	603	604	605	606	607	608	609	610	611	612
613	614	615	616	617	618	619	620	621	622	623	624
625	626	627	628	629	630	631	632	633	634	635	636
637	638	639	640	641	642	643	644	645	646	647	648
649	650	651	652	653	654	655	656	657	658	659	660
661	662	663	664	665	666	667	668	669	670	671	672
673	674	675	676	677	678	679	680	681	682	683	684
685	686	687	688	689	690	691	692	693	694	695	696
697	698	699	700	701	702	703	704	705	706	707	708
709	710	711	712	713	714	715	716	717	718	719	720
721	722	723	724	725	726	727	728	729	730	731	732
733	734	735	736	737	738	739	740	741	742	743	744
745	746	747	748	749	750	751	752	753	754	755	756
757	758	759	760	761	762	763	764	765	766	767	768
769	770	771	772	773	774	775	776	777	778	779	780
781	782	783	784	785	786	787	788	789	790	791	792
793	794	795	796	797	798	799	800	801	802	803	804
805	806	807	808	809	8010	8011	8012	8013	8014	8015	8016
8017	8018	8019	8020	8021	8022	8023	8024	8025	8026	8027	8028
8029	8030	8031	8032	8033	8034	8035	8036	8037	8038	8039	8040
8041	8042	8043	8044	8045	8046	8047	8048	8049	8050	8051	8052
8053	8054	8055	8056	8057	8058	8059	8060	8061	8062	8063	8064
8065	8066	8067	8068	8069	8070	8071	8072	8073	8074	8075	8076
8077	8078	8079	8080	8081	8082	8083	8084	8085	8086	8087	8088
8089	8090	8091	8092	8093	8094	8095	8096	8097	8098	8099	80100
80101	80102	80103	80104	80105	80106	80107	80108	80109	80110	80111	80112
80113	80114	80115	80116	80117	80118	80119	80120	80121	80122	80123	80124
80125	80126	80127	80128	80129	80130	80131	80132	80133	80134	80135	80136
80137	80138	80139	80140	80141	80142	80143	80144	80145	80146	80147	80148
80149	80150	80151	80152	80153	80154	80155	80156	80157	80158	80159	80160
80161	80162	80163	80164	80165	80166	80167	80168	80169	80170	80171	80172
80173	80174	80175	80176	80177	80178	80179	80180	80181	80182	80183	80184
80185	80186	80187	80188	80189	80190	80191	80192	80193	80194	80195	80196
80197	80198	80199	80200	80201	80202	80203	80204	80205	80206	80207	80208
80209	80210	80211	80212	80213	80214	80215	80216	80217	80218	80219	80220
80221	80222	80223	80224	80225	80226	80227	80228	80229	80230	80231	80232
80233	80234	80235	80236	80237	80238	80239	80240	80241	80242	80243	80244
80245	80246	80247	80248	80249	80250	80251	80252	80253	80254	80255	80256
80257	80258	80259	80260	80261	80262	80263	80264	80265	80266	80267	80268
80269	80270	80271	80272	80273	80274	80275	80276	80277	80278	80279	80280
80281	80282	80283	80284	80285	80286	80287	80288	80289	80290	80291	80292
80293	80294	80295	80296	80297	80298	80299	80300	80301	80302	80303	80304
80305	80306	80307	80308	80309	80310	80311	80312	80313	80314	80315	80316
80317	80318	80319	80320	80321	80322	80323	80324	80325	80326	80327	80328
80329	80330	80331	80332	80333	80334	80335	80336	80337	80338	80339	80340
80341	80342	80343	80344	80345	80346	80347	80348	80349	80350	80351	80352
80353	80354	80355	80356	80357	80358	80359	80360	80361	80362	80363	80364
80365	80366	80367	80368	80369	80370	80371	80372	80373	80374	80375	80376
80377	80378	80379	80380	80381	80382	80383	80384	80385	80386	80387	80388
80389	80390	80391	80392	80393	80394	80395	80396	80397	80398	80399	80400
80401	80402	80403	80404	80405	80406	80407	80408	80409	80410	80411	80412
80413	80414	80415	80416	80417	80418	80419	80420	80421	80422	80423	80424
80425	80426	80427	80428	804							

組成 (重量部)		黒鉛粉				
(A) 成分	A-1	29	39	31	32	
(B) 成分	ニッカガラス化成(株) ⁽¹⁾ ニッカガラス化成(株) ⁽²⁾	日本化成塗料(株) 日本化成塗料(株)	6.6	6.6	5.6	5.6
(C) 成分	ラクリアミン	0.66	0.66	0.66	0.66	
皮膜時間 (23°C)	41min	21min	30min以上	105min		

(1) : 2-エチルヘキサン酸銀のミネラルスピリット溶液、金属(作) 含有量 : 6 %
 (2) : 2-エチルヘキサン酸カルシウムのミネラルスピリット溶液、金属(作) 含有量 : 5 %

[0186] As shown in Table 5, the polyoxyalkylene series polymer (A-3; working example 30 and 32) which has a trimethoxysilyl group had the cure rate quicker than the polyoxyalkylene series polymer (A-1; working example 29 and 31) which has a methyl dimethoxy silyl group.

[0187] The same hardenability constituent as working example 6-15 can be prepared using the polyoxyalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3. The tack free time of this constituent has short cure time, and good physical properties are acquired.

[0188] (Constituent which used the epoxy resin together)

The same hardenability constituent as working example 6-15 can be prepared using the constituent which used together reactive silicon group containing organic polymer and an epoxy resin. When this constituent is used, the manifestation of adhesive strength is quick.

[Industrial applicability]

[0189]

(A) The organic polymer which has the hydroxyl group or hydrolytic basis combined with the silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond. (B) Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium. The hardenability constituent containing one or more sorts of carboxylic acid metal salt which it comes to choose out of carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, While revealing practical hardenability and stability, the hardened material obtained shows the outstanding mechanical physical property which has high intensity and high elongation as compared with the case where the carboxylic acid tin currently used conventionally is used as a curing catalyst. Therefore, the hardenability constituent of this invention is very useful as various elastomers, such as a sealing material, adhesives, a binder.

[Translation done.]